A NEW METHOD FOR THE PREPARATION OF POLY(SILMETHYLENE) AS A PRECURSOR FOR SILICON CARBIDE FIBERS

Maher Abu-Eid[1]

ملخص

لقد تم تحضير بولي سيلمثيلين من ٣ كلوريد بروبيل ثلاثي كلوروسيلان ومن ثم دراسة التركيب البنائي لهذا البولمر باستخدام جهاز الأشعة تحت الحمراء وجهاز تردد الطيف المغناطيسي. هذا وقد تم دراسة عملية تكسير البولمر باستخدام جهاز التحليل الحراري الوزني ووجد ان كمية انتاج السيراميك لهذا البولمر تصل الى حوالي٧٠ ٪ عند درجة حرارة ٩٠٠م°.

ABSTRACT

Poly(silmethylene) has been prepared form 3-chloropropyltrichlorosilane. The structure of poly(silmethylene) was investigated by IR and NMR spectroscopy. The pyrolysis of the polymer was studied by Thermal Gravimetric Analysis (TGA) and was found to give 70% ceramic yield after pyrolysis temp. of 900°C.

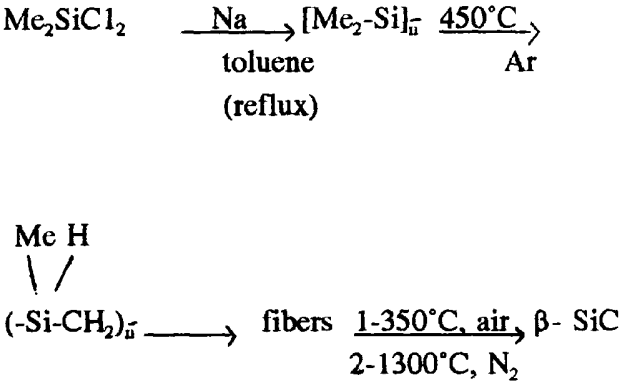
INTRODUCTION

There has been a great deal of interest in recent years[1,6] in the use of polysilanes and polycarbosilanes as precursors for ceramic materials. The importance of ceramic fibers comes from the fact that they offer a great promise as light weight construction materials in applications where high strength and modulus are required at elevated temperatures.

1 Chemistry Department,An-Najah N. University Nabuls West-Bank

The controlled pyrolysis procedure of polydimethylsilane can produce silicon carbide fibers[7,11]. Yajimas pyrolysis procedure shown in Scheme I makes such fibers readily available and such fibers under the name Nicalon are currently being produced by Nippon Carbon |Dow-Corning.

Scheme I:

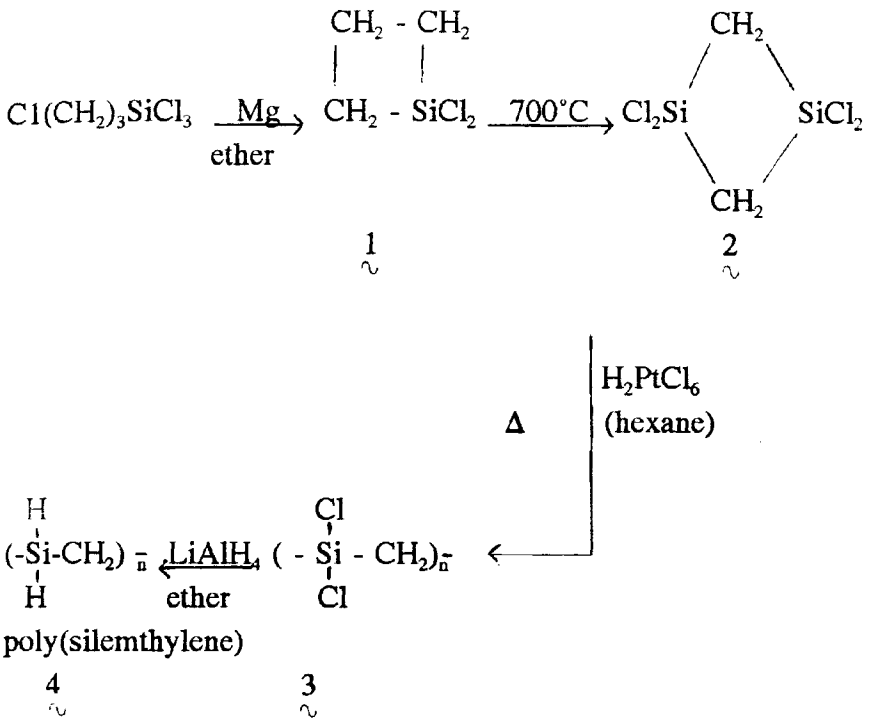


However, the process of Yajima still suffers from low ceramic yield[8,9] and from the necessity for lengthy and multistage processing.

In this article, a new method has been developed for the production of silicon carbide based on the pyrolysis of poly-(silmethylene). The results of the efforts to employ 3-chloropropyltrichlosilane as a starting material for the preparation of

poly(silmethylene), 4, are presented, Scheme II. The structural and thermal properties of the polymer 4 are also discussed.

Scheme II:



EXPERIMENTAL

Materials :

Commercially available ether and hexane were distilled over sodium and benzophenone. All other chemicals were used as obtained commercially.

Instruments :

The ^1H NMR spectra were obtained by using 250 MHZ Bruker spectrometer with $CDCl_3$ as solvent and internal standard. The FT-IR spectra (KBr disc) were obtained by using a Nicolet 60 SX system. TGA was carried out by using a Perkin Elmer 7 Series with heating rate of 10°C| min under nitrogen.

Preparation of 1,1-dichloro-1-silacyclobutane (1):

As shown is Scheme II, 1 was prepared according to the following procedure[12]: A 2 liter three-necked round-bottomed flask was fitted with a nitrogen by-pass, and a mechanical stirrer. To this apparatus 800 ml of ether and 44g of magnesium were added. 217g of 3-chloropropyl-trichlorosilane was added slowly over a period of 4 hours maintaining the ether under gentle reflux. Heating and rapid stirring of the mixture was maintained for 120 hours. The flask was allowed to cool and the magnesium chloride and excess magnesium were separated by filtration through a large sintered glass filter. 1 was obtained in 54% yield after distilling the filtrate. B.p. (112-115°C). ^1H NMR ($CDCl_3$) δ1.85 ppm (triplet, 4H), 2.01 ppm (quintet, 2H).

Preparationof1,1,3,3-tetrachloro-1,3-disilacyclobutane,(2):

The preparation was performed by pyrolysis of 1 using a Vycor tube packed with procelain chips and heated to 700°C[13]. The Vycor tube was connected to a series of 3 cold temperature traps. The pyrolysis was performed under vacuum. 42 g of 1, were introduced at the rate of 3ml|hour. The pyrolysis products were collected as white solid materials in the absence of air. Due to the high sensitivity

of the reaction products, their color changed from white to brown when exposed to air.

Distillation of the products collected under nitrogen gave the tetrachloride (bp 165°C) in 53% yield. ^1H NMR ($CDCl_3$) δ 1.91 ppm (singlet).

Ring-Opening Polymerization of 2:

To 6.5 g of the tetrachloride in 50 ml dry hexane was added 0.935 g of $H_2PtCl_6 . 6H_20$. The solution was refluxed under nitrogen for 24 hours. The solvent was removed by vacuum to yield a viscous brown polymer which was used directly in the following reaction without further purification.

Reduction of Poly[(dichlorosilylene) methylene], 3 :

The polymer 3 obtained from the previous reaction was dissolved in 60 ml of ether. A mixture of 0.59 g of $LiAlH_4$ in 40 ml of ether was added slowly to the polymer solution via syringe with proper stirring under nitrogen. After the addition of $LiAlH_4$, the solution was stirred for 24 hours at room temperature. The excess of $LiAlH_4$ was removed by addition of 2M HCl. The ether layer was separated and the ether removed under vacuum to yield a light yellow polymer. (yield 83% based on poly [(dichlorosilylene) methylene], 3).

RESULTS AND DISCUSSION

In the initial stages of this work, an attempt has been made to prepare poly(silmethylene), 4, via the direct synthesis of chloromethyltrichlorosilane with magnesium and then reducing the filtrate of Grignard reaction by $LiAlH_4$[14,15]. The ^1H NMR spectra for the white viscous material obtained suggest the formation of carbosilane polymer with other linear and syclic oligomers. The formation of a variety of products by such reaction was similar to the results reported by Kriner[14] and Seyferth[16].

A new method has been developed in this work for the production of poly(silmethylene), 4, from 3-chloropropyltrichlorosilane as the starting material. The method is summarized earlier in Scheme II.

In the procedure used to prepare 1, the yield of this reaction is affected greatly by the speed and time of stirring. Yield of 21% was obtained by stirring for 2 days whereas vigrous stirring for 5 days gave 54% yield of 1. The preparation of 2 was performed by pyrolysis of 1 under vacuum instead of pyrolysis under nitrogen as described by Nametkin[13].

It was found from many trials that pyrolysis under vacuum gave better yield of 2 and was much easier to proceed. The structure of 2 was confirmed by ^1H NMR and was found similar to that reported by Grobe[17]. When 2 was mixed with H_2PtCl_6 and refluxed to 80°C, a gradual increase in viscosity of the mixture was observed which

indicates the occurance of ring opening polymerization as reported by Seyferth[17], for other carbosilane polymers. The IR spectrum of 3 showed strong bands at 1350 and 1040 cm^{-1} due to $Si-CH_2Si$ deformation. Only a single peak was observed by ^1H NMR at 1.89ppm for this polymer.

After reduction of 3 with $LiAlH_4$, dilute hydrochloric acid was added to separate the salts. The addition of aqueous hydrochloric acid to the polymer 4 solution did not hydrolize the Si-H bonds as indicated by the results of IR (Table I) and the ^1H NMR spectra (Figure 1). The stability of Si-H bonds to aqueous mineral acids is well known[18].

Table 1: Infrared Absorption Spectra for Poly(silmethylene)

Wave number cm^{-1}	Assignment
2960(w)	CH_2 stretching
2138(vs)	Si-H stretching
1090(vs), 1354(s)	$Si-CH_2-Si$ deformation
810(vs)	Si-H bending
790(vs)	Si-C stretching

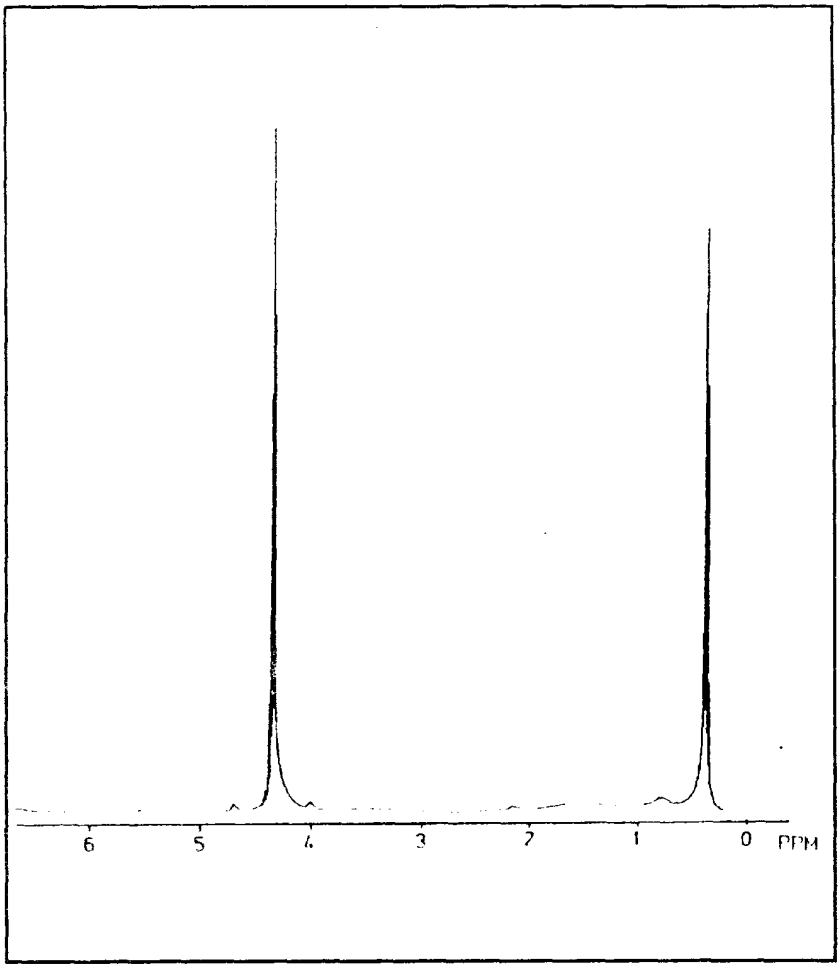


Figure 1 : ^{1}H NMR spectra of poly(silmethylene), 4.

Thermogravimetric analysis was performed on samples of poly[silmethylene] 4 and on polydimethylsilane, 5, -[Me_2Si]$_n$, prepared according to the method of Backard[19]. The curves are shown in Figure 2.

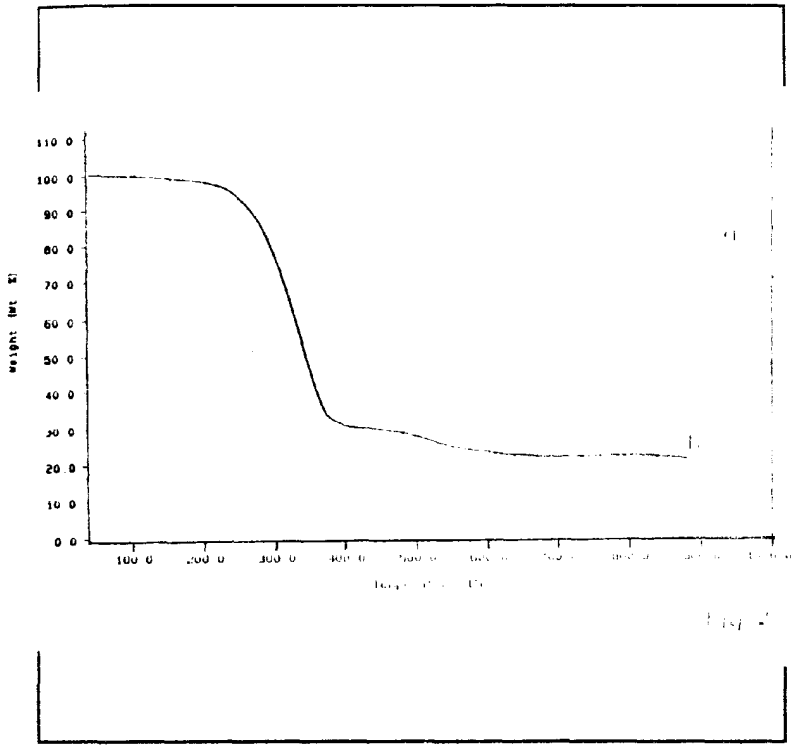


Figure 2 : TGA plot of poly(silmethylene), 4, (a), and TGA plot of polydimethylsilane, 5, (b).

Polydimethylsilane, 5, loses 76% of its weight upon heating under nitrogen up to 900°C, whereas polysilmethylene, 4, loses 21% of its weight. The high ceramic yield obtained from polysilmethylene compared to that of Yajimas method[9] indicates the importance of polysilmethylene as a precursor to silicon carbide fibers.

ACKNOWLEDGEMENT

Advice and help from Prof. R.B. King, University of Georgia, Athens, U.S.A, is greatly appreciated.

REFERENCES

1. West, R., David, L., Djurovich, P., Yu, H. and Sinclair, R., (1983), Ceramic Bulletin, 62: 899.
2. Qiu, H. and Du, Z., (1989), J. Polym. Sci., 27: 2849.
3. Yajima, S., Hagashi, J. and Omori, M., (1975), Chem. Lett.: 931.
4. Yajima, S., Iwai, T., Yamamura, T., Okamura, K. and Hagashi, Y., (1981), J. Master. Sci., 16 : 1349.
5. Abu-Eid, M., King, R. and Kotliar, A., (1992), Europ. Polym. J., 28 : 315.
6. Yajima, S., Hasegawa, Y., Hayashi, J. and Ilmura, M., (1978), J. Mater. Sci, 13 : 2569.
7. Hasegawa, Y., Ilmura, M. and Yajima, S., (1980), J. Mater. Sci., 15 : 720.
8. Hasegawa, Y. and Okamura, K., (1983), J. Mater. Sci., 18 3633.
9. Yajima, S., Hayashi, J., Omori, M, (1978), U.S. Patent 4, 100, 233.
10. Koga, K., Nagano, S., (1978), U.S. Patent 4, 105, 455.
11. Yajima, S., Hayyashi, J., Omori, M, (1977), U.S. Patent 4,052, 430.
12. Lanne, J., (1967), J. Am. Chem. Soc., 89 : 1144.
13. Nametkin, N., Vudovin, V., Zavyalov, V. and Gninberg, P., (1965) Izv. Akad. Nauk, SSSR, Ser. Khim.: 929.
14. Kriner, W. (1964), J. Org. Chem., 29: 1601.
15. Nametkin, N., Vdvin, V., Zavyalov, V and Garinberg, P., (1964), Izv. Akad, Nauk, SSSR, Sor. Khim., 5 : 929.

16. Seyferth, D., (1988), Inorganic and Organometallic Polymers, ACS, Washington, DC, 3 : 21.
17. Auner, N. and Grobe, J., (1980), J. Orgonometal, Chem., 188 : 151.
18. Cotton, F.A. and Wilkinson, G., (1988), "Advanced Inorganic Chemistry", 5th ed., J. Wiley, N.Y., P. 275.
19. Burkhard, C., (1949), J. Am. Chem. Soc. 71, 963.